

**Changes in the Wave-Frequencies of the Lines
of Emission Spectra of Elements, their De-
pendence upon the Elements themselves
and upon the Physical Conditions
under which they are Produced.**

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BY



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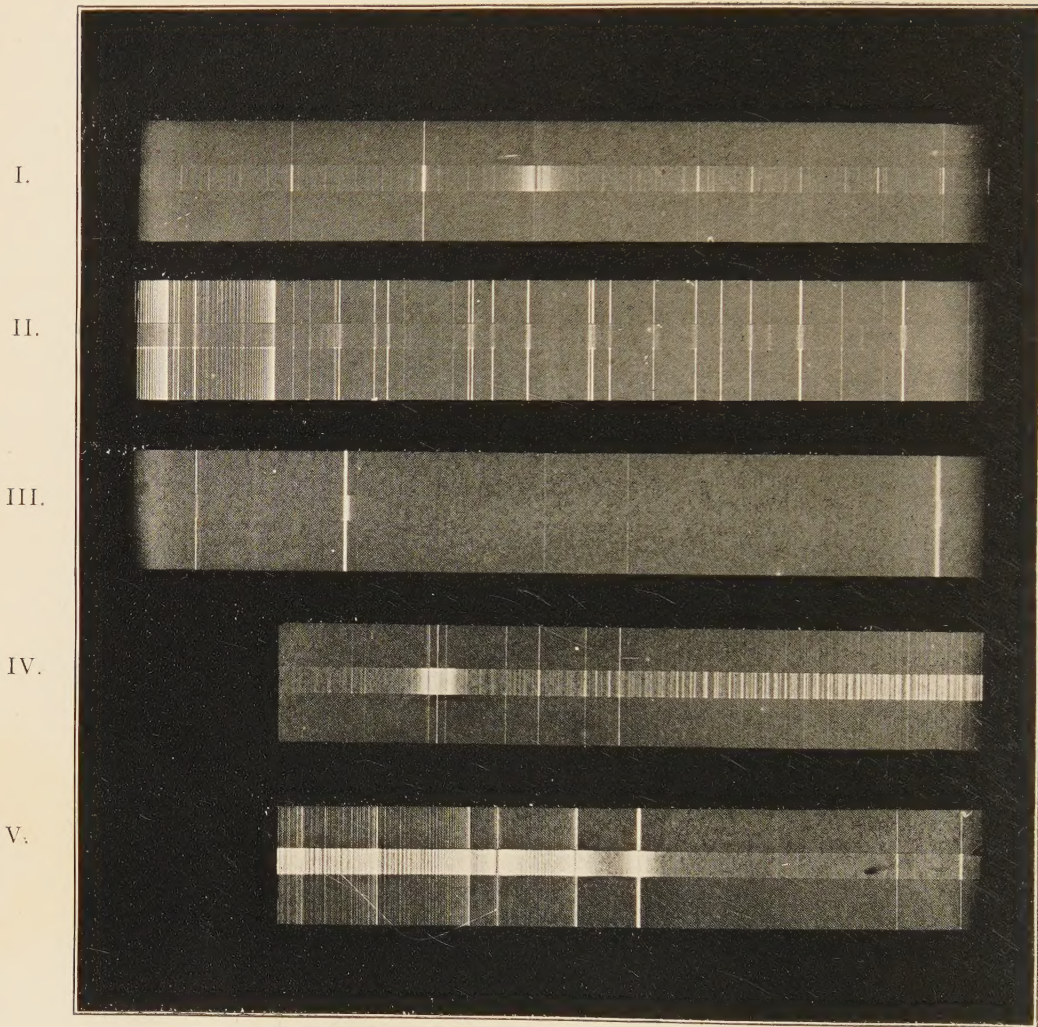
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PLATE XVII.



SHIFTS OF SPECTRAL LINES DUE TO PRESSURE

- I. A pair of sodium lines which widen toward the violet, but shift toward the red.
- II. New Concord Meteorite. All the iron lines are not equally shifted. Cyanogen bands unaffected.
- III. Two classes of copper lines having different shifts.
- IV. Large shifts of two potassium lines.
- V. Shifts of the rubidium lines in the cyanogen band.

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By W. J. HUMPHREYS.

PRELIMINARY REMARKS.

It is well known to spectroscopists that the character of the emission spectrum of an element depends greatly upon the physical conditions under which it is produced. If the element is in the solid or liquid state its spectrum is continuous, but discontinuous when it is in the form of an attenuated gas. The discontinuous spectrum may consist either of bands or of isolated lines or of both, according in part to the substance used, and in part to the conditions under which its spectrum is formed. In general the number of lines that can be detected and their intensities increase with increase of temperature, though their relative intensities may change very greatly as the temperature is raised. Increase in the density of a gas or vapor increases the width of its spectral lines; some of them spread out symmetrically, others unsymmetrically. In the latter case the chief increase in width is usually, but not always, towards the less refrangible or red

end of the spectrum. A somewhat similar increase in the width of lines (both emission and absorption), together with certain polarization phenomena, may be produced, according to Zeeman,¹ by placing the vapor to which the lines are due in a strong magnetic field.

Again, whether a line is reversed or not depends in part at least upon the thickness and density of the absorbing layer. Finally a single element, as argon for instance, may give one or another of two distinct line spectra owing to the character of the electric discharge used to produce it, and to the pressure of the gas.

Not only emission but absorption spectra also are known to be subject to changes. One of the most important of these changes was observed by Kundt who, in describing it, says that the position of an absorption band depends upon the substance in which it is dissolved or incorporated, that the band is displaced towards the red end of the spectrum when the substance producing it is dissolved in a strongly dispersive medium; or, to use his own words, as they occur in an article on absorption spectra.² "Hat ein farbloses Lösungsmittel ein beträchtlich größeres Brechungs- und Dispersionsvermögen als ein anderes, so liegen die Absorptionsstreifen einer in den Medien gelösten Substanz bei Anwendung des ersten Mittels dem roten Ende des Spectrums näher als bei Benutzung des zweiten."

In view of the reciprocal relation between absorption and emission of radiations, it would seem that one might suspect the possibility of a similar phenomenon, that is shift of lines, in the case of emission spectra. Indeed some observers have reported shifts of certain spectral lines, and besides something of the kind is suggested by the theories of both Lommel³ and Wüllner.⁴

¹ "On the influence of Magnetization on the Nature of the Light Emitted by a Substance."—*Phil. Mag.*, March 1897; this JOURNAL, 5, 332, 1897.

² "Ueber den Einfluss des Lösungsmittels auf die Absorptionsspectra gelöster absorbirender Medien."—*Wied. Ann.*, 4, 34.

³ "Theorie der Absorption und Fluorescenz."—*Wied. Ann.*, 3, 251.

⁴ "Ueber almähliche Ueberführung des Bandenspectrums des Stickstoffs in ein Linienspectrum."—*Wied. Ann.*, 8, 590.

However, these observations were all but certainly illusive, as others have asserted, and as will be explained further on, and the theories are at least incomplete since they do not agree in all respects with observations. In considering them I shall confine myself to those parts that deal with the displacements or shifts of the lines.

According to Lommel's theory the spectral lines increase in width, chiefly on the red side, and shift in the same direction when the density of the gas producing them is increased. He says: "*Bei vergrößerung der Dichte oder des Drucks eines Gases erleidet die helle Spectrallinie eine Verbreiterung und gleichzeitige Verschiebung nach der weniger brechbaren Seite hin.*"

This theory makes the spreading of a line and its displacement depend upon the same thing—namely, the increase of the density of the gas whose lines are affected. According to it the spreading must always be chiefly towards the red end of the spectrum, and the lines must shift only when they are spread out; in fact the shift of a line is due, in terms of the theory, to unsymmetrical broadening and to nothing else.

As a matter of fact, while many lines are spread out, by increase of the density of the gas producing them, chiefly towards the red end of the spectrum, many others are broadened symmetrically, and others even spread out chiefly towards the more refrangible or violet end. Therefore by merely increasing the density of the luminous gas or vapor, without change of total pressure, the centers of certain lines are moved toward the red and others toward the violet of the spectrum; while those lines that spread symmetrically are not displaced at all. Besides the reversals, which of course give the positions of the most intense portions of the lines, are never displaced in the slightest by any increase in the density of the luminous gas or vapor so long as the absolute pressure is kept the same.

The shift discussed in this paper probably does not depend in the least, as will appear from the experimental results, upon the density of the gas or vapor producing the lines, but only

upon the absolute pressure; and apparently it has no connection with the spreading, either symmetrical or unsymmetrical, of the lines themselves. It would therefore seem that Lommel's theory, though ingenious and well worked out, in no wise predicts the observations described in the following pages.

In support of that part of his theory which demands a shift of the lines, Lommel refers to the experiments of Zöllner¹ and Müller,² both of whom used the common method of putting a bead of salt in a Bunsen flame and then examining, by suitable methods, the light so produced. The intensity of the flame and the quantity of salt in it were both varied, and some of the results they obtained indicated a movement of the lines towards the red end of the spectrum. This can be explained by, and was almost certainly due to, unsymmetrical spreading of the lines examined. Certainly neither observer found (the conditions were not such as would produce it) a true displacement of the lines in the sense that the term is used in this paper. That is, they did not find a given line, produced under certain conditions, differing from the same line when produced under other conditions in any wise except mere position in the spectrum; nor do they speak of the displacement of the reversals.

The other theory referred to, that of Wüllner, assumes all variations in the spectrum of a substance to be due to what might be termed external changes, such as temperature, density, and the like, and in no case, not even in the change from band to isolated line spectra, to any alteration of molecular grouping. Wüllner assumes the correctness of Zöllner's equation,

$$E = \left\{ 1 - (1 - a)^{d\delta} \right\} e,$$

in which E is the total amount of light of a given wave-length, d the thickness, δ the density, a the coefficient of absorption of the luminous gas or vapor, and e the power of a perfectly black

¹"Ueber den Einfluss der Dichtigkeit und Temperatur auf die Spectra glühender Gase." *Pogg. Ann.*, **142**, 88.

²"Beobachtungen über die Interferenz des Lichtes bei grossen Gangunterschieden." *Pogg. Ann.*, **150**, 311.

body, at the same temperature as the luminous gas, to give out light of the given wave-length. If a is a function not only of wave-length but of temperature too, and such a function of them that its maximum value occurs at different places for different temperatures, as Wüllner assumes it to be, then clearly a line may be shifted by merely changing the temperature of its source. Besides, the shift may be in either direction and may be regular or irregular. In short, if a is such a function of temperature and of wave-length as that just described one can only say that a given change in temperature will produce a greater or less change, in one direction or the other, in the position of a line in the spectrum. In certain respects the conclusions of this theory are not supported by careful observations, and for this reason it is not now, if ever, well received by spectroscopists. In regard to the displacements of the lines it is stated by Kayser,¹ in an article in which he discusses the above theory quite fully, that he knows of only one line, D_2 , of which accurate measurements have indicated a shift, and that in this case the shift is illusive, and due to unsymmetrical broadening. His words are: "Mir ist nur ein Fall bekannt wo man nach genauen Messungen eine Verschiebung glaubte beobachten zu können: nämlich bei der Linie D_2 ; aber dies ist, wie an anderer Stelle gezeigt werden soll, eine Täuschung: D_2 verbreitet sich nicht gleichmässig nach beiden Seiten, daher scheint sich die Mitte etwas zu verschieben, aber der hellste Theil, die eigentliche Linie bleibt genau an ihrer Stelle." In another place² Kayser says that neither lines nor bands have ever been observed to shift. "Eine Verschiebung von Linien ist selbst von den genauesten Messungen niemals beobachtet worden, weder beim Banden- noch beim Linienspectrum."

Before the present work was begun no accurate experiments, so far as I can learn, had shown a true shift independent of all other changes of the spectral lines, nor had it been demanded by theory. Lommel's theory made the shifts of the lines a conse-

¹ "Ueber den Ursprung des Banden- und Linien Spectrums." *Wied. Ann.*, 42, 310.

² WINKELMANN, *Handbuch der Physik*, II, 1, p. 425.

quence of their unsymmetrical spreading, while Wüllner's theory, though capable of explaining any one of several phenomena, is too flexible to predict shifts of lines at all definitely. It only states in this particular what is perfectly evident, namely, that by changing the conditions under which the spectrum of a substance is produced its lines may or may not be displaced, which of course is really predicting nothing.

As stated above, neither of these theories has been supported as to the shifts of the lines by observations. Instead then of regarding the wave-frequency of a line, and consequently its wave-length and position in the spectrum, as being one thing or another, owing to circumstances, practically all spectroscopists have considered it a constant of reference (except as modified by the Doppler effect), subject to no possible change. All observers who have given us tables of accurately determined wave-lengths have, at least tacitly, made this assumption, and upon it are based the estimates of the velocities in the line of sight of many of the fixed stars. The same assumption is made in comparing solar and stellar with terrestrial spectra for the purpose of determining the constituents of the Sun and stars, and when the coincidence of lines evidently the same was not exact the discrepancy was naturally referred to some cause other than actual change in wave-length.

This assumption of the constancy of wave-frequency has led to the hope, a vain one it seems, that wave-lengths of spectral lines may serve as ideal units of reference—units whose values are absolutely the same at all times and under all circumstances.

While the wave-frequencies of spectral lines depend, as shown further on in this paper, upon the physical conditions under which they are produced and therefore their wave-lengths are not ideal units of reference, still it is easy to obtain spectral lines, as often as desired, under conditions so similar that their wave-lengths are more nearly ideal length units than are those which we can at present obtain in any other way. Consequently the results of the experiments described in the following pages do not materially affect (though they show precautions that must

be taken) the value of Professor Michelson's¹ most ingenious and careful determination of the wave-lengths of the red, green, and blue lines of the spark-spectrum of cadmium vapor at low pressure, in terms of the standard meter.

OBJECT OF THE INVESTIGATION.

The work described in this paper was suggested by Dr. Ames and begun for the purpose of examining minutely the effect of pressure on the arc spectra of various elements, and in particular for noting the effect if any on the wave-lengths of the lines. The idea of examining arc spectra under pressure occurred to Professor Rowland several years ago, and the apparatus used in the present investigation is that which he had constructed for this purpose. Constant work however along other lines prevented him from making any observations with it.

The first accurate observations, to the best of my knowledge, that suggested the probability of a functional relation between the wave-frequencies of spectral lines and the conditions under which the lines are produced were made by Mr. L. E. Jewell in the physical laboratory of the Johns Hopkins University. The suggestion came in part from the fact that Mr. Jewell's numerous and careful measurements of the same lines in the arc and solar spectra showed a want of coincidence which varied for different elements. While this want of coincidence was never great, still it seemed too regular to admit of the apparently obvious explanation that it was not due to any real difference in wave-length, but to some disturbance of the apparatus during the exposure of the photographic plate. Mr. Jewell had also obtained slight real or apparent displacements of certain lines by changing the amount of material in the arc. It was this chiefly that led Dr. Ames to suggest the present investigation.

The only way, of course, to determine whether such a functional relation between wave-lengths of spectral lines and the conditions under which the spectra are produced actually exists,

¹"Determination experimental de la valeur du mètre en longueurs d'ondes lumineuses."

was by direct experiment, and it therefore seemed advisable to examine arc spectra under different conditions, especially of pressure and so far as possible of temperature too, since the conditions under which solar and ordinary spectra are produced may differ greatly in both these respects.

Another reason for taking up this investigation was found in the fact that the wave-lengths of the red, blue, and green cadmium lines as determined by Professor Michelson for the purpose of accurately comparing them with the standard meter, were less in each case than those of the same lines as determined by Professor Rowland. These differences are .208 of an Ångström unit for the red, .173 for the green, and .186 for the blue line. In each case the difference amounts to only about one part of the wave-length in thirty thousand, and in itself is not very surprising, since the methods followed by these two able men were totally different; but it is rather surprising that these differences are not constant. Here again differences of physical conditions under which the spectra were produced (Michelson worked with spark spectra at low pressure, while Rowland used the arc at atmospheric pressure) suggest a possible explanation of the want of agreement in their measurements. The results of numerous examinations of cadmium spectra as produced under different pressures do account for a part, though only about 5 per cent., of the above differences, but fail to suggest, at least very definitely, why the differences should not be the same for all the lines.

APPARATUS USED.

The grating used in all this work was a six-inch Rowland concave of twenty-one and a half feet focal length and ruled with 20,000 lines to the inch. It was mounted in the usual way, as fully described by Dr. Ames in the *Johns Hopkins Circular* of May 1889. The arc was produced by a direct 110-volt current of any amperage desired. It was found necessary to make the strength of the current very different for different substances and also for different amounts in the arc of the same substance. At times the current was small—only a few amperes—while occasion-

ally, judging from the fuses blown and other effects, it was little if any less than one hundred. The effect of varying the strength of the current will be discussed further on. The poles of the electric arc were used vertical and parallel to the slit of the spectroscope. Horizontally mounted poles were also tested, and the results will be given in the proper place, but it did not appear necessary to use any other than the vertical mounting, which was found to be much the more convenient of the two tried.

A number of photographs were taken of the spectrum given by an arc between one carbon and one (the lower) metallic pole, and a few of the spectrum formed by an arc between two metallic poles. The metals so used were iron, copper, brass and zinc. In all other cases both poles were of carbon, the lower one being bored axially to a depth of from one to three inches. This cavity, which was about an eighth of an inch in diameter, was filled with the substance or substances whose spectrum was desired. Very often elements were used in the metallic form, but as a rule it was more convenient and occasionally, as in the case of sodium and potassium, much better to use some compound. The quantity of the element or compound in the arc could easily be reduced, as was often necessary, by mixing it with carbon dust before charging the pole with it. In nearly all cases the pole carrying the charge was made the positive one.

The pressure around the arc was obtained in every instance by pumping air into the apparatus designed for this work by Professor Rowland, as stated above, and used by Messrs. Duncan, Rowland and Todd¹ in their examination of the electric arc under pressure. The structure of this apparatus may be understood by aid of the accompanying sketch, Fig. 1, in which *A* is an iron cylinder fourteen inches high and seven inches in diameter. *B*, *B* are suitably constructed stuffing boxes through which the rods *C*, *C* pass practically air-tight. These rods are insulated from the smaller rods *H*, *H* which they contain, and which carry the carbons. *N* is the negative and *P* the positive

¹ *Electrical World*, 22, 1893.

pole as commonly used. The latter is represented partly in section to show the cavity *S* in which the substance whose spectrum is desired is placed. The carbon *N* can be raised and lowered by means of the rack *R* and pinion *G*, and the carbon

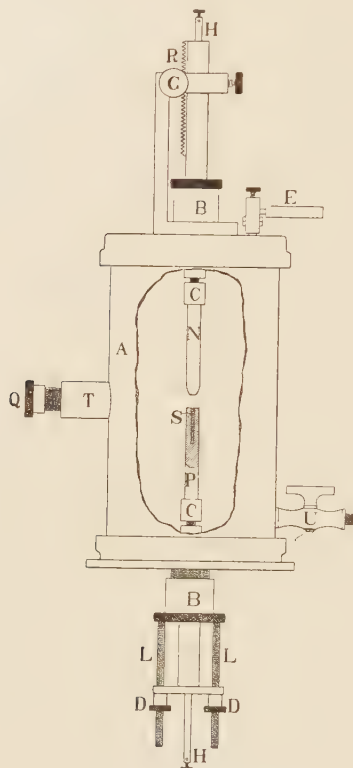


FIG. 1.

P can be brought to the proper position with the nuts and screws *D, D* and *L, L*. The light reaches the slit of the spectroscope by passing through the side tube *T*, which is closed at *Q* with a plane quartz disk. The object in using quartz instead of glass is of course to avoid, as far as possible, the absorption of the ultra-violet light. The air is pumped in through the tube *U*, which can be opened and closed by means of the stopcock *V*,

and the pressure is given by a Bourdon gage E , reading from one to twenty atmospheres.

METHOD OF PHOTOGRAPHING.

For the purpose of accurate comparison it was necessary to obtain side by side photographs of the spectra of the substance in question as given by the arc under the two pressures used, the lowest of which was always that of one atmosphere. It was also necessary to guard, as far as possible, against any accidental movement of the camera or other part of the apparatus during the exposure and to be able to surely detect any such accidental disturbance should it occur, since any slight movement of the apparatus during, and especially between successive exposures on the same plate, would necessarily lead to false results.

The first of these requirements, that is the obtaining of the spectra in such way that they could be accurately compared, was met in the same manner (and with the same apparatus) that Professor Rowland met a similar requirement in the comparison of solar and arc spectra, that is by providing the camera, which takes a nineteen by one and a quarter-inch plate, with a rotating shutter so constructed that in one position it shields the sides along the entire plate and leaves a narrow middle strip exposed, while in a certain other position it shields the middle strip and exposes the sides. In nearly every case the middle strip was exposed to the arc under pressure, after which the air was let out from the cylinder, the shutter adjusted and the sides of the plate exposed to the arc at atmospheric pressure.

The method used at first for detecting accidental disturbances was as follows: By means of an auxiliary shutter a small portion of the middle strip was exposed to the solar spectrum, all other parts of the plate being shielded, then the remainder of this strip to the arc under pressure, then the corresponding sides to the arc at atmospheric pressure, and finally the remaining portions to the solar spectrum. This process secured a short section of solar spectrum, the middle portion of which was exposed

before, and the sides after the exposures to the arc. Consequently any disturbance of the apparatus between the first and last exposures was shown by breaks in the solar lines. It soon became evident, however, that this method, though accurate, was not necessary, since the lines of the carbon bands, some of which occur on nearly every plate, are never measurably displaced, and therefore serve perfectly to detect any disturbance of camera or other part of the apparatus during or between the exposures.

METHOD OF MEASURING.

The shifts of a few lines were determined by direct observations with a micrometer eyepiece, but in all other cases the measurements were carefully made on photographs with a most accurate dividing engine especially constructed by Professor Rowland for this sort of work, and used in determining Rowland's Table of Standard Wave-lengths. The dividing engine and the micrometer eyepiece are both constructed to read directly to hundredths of a millimeter, and may be estimated to thousandths of a millimeter.

Most of the plates were taken in the second spectrum, where the dispersion is a little more than one millimeter per Ångström unit, though a few were taken in the first, where the dispersion is one-half that of the second, and many in the third, where it is three halves that of the second. In all several hundred negatives were secured and the shifts determined of those lines whose positions were well defined by reason either of their sharpness or of their reversals.

To facilitate the measuring of the shifts and at the same time to increase the accuracy a system of double cross-hairs was placed, as shown in Fig. 2, in the field of the microscope. In the process of measuring the microscope was kept fixed and the negative moved along by the micrometer screw until the cross *a* was on the center of a given line in the middle strip, that is a line produced by the arc under pressure, when a reading was taken. The plate was then moved forward by the screw

until the crosses bb were on the center of the same line as formed on the sides of the plate by the arc at atmospheric pressure, when another reading was taken, and so on for other lines. The plate was then reversed and the same process repeated.

Let s be the shift of any line, and l the difference in readings that would be given by the crosses a and bb when there is no

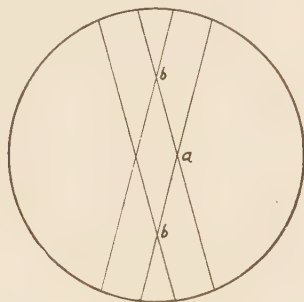


FIG. 2.

shift, and let the direct reading of the crosses bb be λ and the reversed d . By "direct reading" is meant that which is obtained when the plate is being moved so that the successive lines to come into the field of the microscope are of increasing wave-length, and by "reversed reading" that obtained when the plate is moving so that the successive lines seen through the microscope are of decreasing wave-length. The direct reading, therefore, given by a is $\lambda - l \pm s$, and the reversed $d - l \mp s$. Evidently $\lambda + d$ is a constant for all the lines on any one plate, from which, if the reversed readings be subtracted, remainders, "corrected reversed," will be obtained equal respectively to λ and $\lambda + l \pm s$. Consequently for any one line the average of the two readings "direct" and "corrected reversed" given by the crosses bb is λ , and that of those given by the cross a , $\lambda \pm s$, their difference being the shift $\pm s$. By this means the accuracy of the measurements is rendered quite considerable. In the case of extra good lines the error should not exceed from two to three thousandths of an Ångström unit.

EXPERIMENTAL RESULTS.

A little preliminary work was done with the arc spectra, at atmospheric pressure, of cadmium and a few other elements. The chief changes found were those of intensity and width of the lines, both of which increased with increase of material. A large amount of material in the arc caused the reversal of many lines, but in every case examined the reversal coincided very closely if not exactly with the position of the corresponding fine lines as produced by a small amount of the substance.

The element whose spectrum as formed under pressure was first examined was cadmium, and it was at once noticed that the positions of its lines were very appreciably changed by a pressure of even three or four atmospheres. Subsequently the lines of a large number of other substances were similarly examined, and in every case their positions, except those of lines of certain bands, were more or less changed.

That this change in position of the lines is not due to any strain or movement of some portion or other of the apparatus may be shown in several ways, but it is easiest and also best shown by the fact that on the same plate lines due to different substances are displaced to very different extents, whereas they should be equally displaced if the displacement were due to a disturbance of the apparatus while photographing. Nor is the observed shift of the lines due to unsymmetrical broadening, since in many cases equally fine and sharp lines were obtained at high and normal pressures, the only important difference between the lines as obtained under the two conditions being that of position. Not only were numerous lines of this character photographed, but the evidence as furnished by the negatives was also checked and confirmed by a number of eye observations, especially on the cadmium lines λ 6438.680 and λ 5086.001, and the sodium lines D_1 and D_2 . By filling the positive pole with fused potassium sulphate, which usually, like the specimen used, contains more or less sodium, it was easy at any pressure, up to ten or more atmospheres, to get the sodium lines D_1 and D_2 , and to retain

them some minutes as beautifully fine and sharply reversed lines, differing in no respect from the same lines as obtained at very different pressures except quite decidedly in position. A further reason for the statement that the shift is not due to unsymmetrical broadening is found in the fact that the wave-lengths of all fine and sharp lines, and also of the reversals of heavy ones, increase with increase of pressure around the arc, no matter how the lines may spread out, symmetrically or chiefly towards either side. A splendid example of this is furnished by the pair of sodium lines λ 3302.504 and λ 3303.119. These lines are quite unsymmetrical—spreading chiefly towards the violet or more refrangible end of the spectrum—but their reversals are greatly shifted in the opposite direction. Neither is the shift due to the disappearance of one line and the appearance of another of slightly different wave-length, because the wave-length increases regularly and not by jumps as the pressure is increased; and, besides, it is not difficult to observe, while the pressure is being slowly let off, either a fine line or the reversal of a heavy one gradually change in position without alteration in width or any other respect.

It has been suggested by Schuster¹ that this shift of spectral lines is possibly due to the “proximity of molecules vibrating in equal periods.” If this supposition is correct, then, of course, the shifts of the lines should be greater at any given pressure, as Schuster says, the greater the amount of material used that produces them. However, many experiments both before and since the appearance of Schuster’s paper show that this is not the case. Among the substances that have been most fully tested in this respect are iron, titanium, copper, and zinc. The carbons used, though reasonably pure, contained a considerable number of impurities in sufficient amounts to give some of their strongest lines, and among these substances were iron, titanium, and copper, each of which gave some very fine but quite measurable lines. The amounts of these substances were then gradually increased until they were as great as possible. In the case of

¹ *Ap. J.*, April 1896.

iron, copper, and zinc, solid rods of the metals were finally used, but in every instance the shift of a given line of any substance remained constant for any definite pressure, showing that it depends upon the absolute pressure and not upon the partial pressure of the gas or vapor producing the line in question.

More recently it has been suggested by Fitzgerald¹ that a "*vera causa* for some shift towards the red in molecules causing light" is the increase of the specific inductive capacity, due to increase of density, of the gas surrounding the arc. This suggestion is based, of course, upon the assumption, possibly a correct one, that "electric forces are at least a part of the forces affecting the periods of vibration." The correctness of this suggestion has not been submitted to actual experimental tests, nor does it seem very easy to do so, at least not directly, since the differences in the specific inductive capacities of gases are not sufficient to produce changes in the shifts greater than the errors of observation, even if the shifts are due entirely to the cause suggested. No matter what theory or suggestion is advanced, it must be remembered that it is imperfect if it does not account in some way for the important fact that at least many elements produce two or more groups of lines, differing greatly from each other in the magnitude of their shifts.

If, as many believe, the temperature of the electric arc is that of boiling carbon it would seem natural to suppose that it would rise with increase of pressure. Very little seems to have been done to test this point, but a number of experiments as conducted by Wilson,² and later by Wilson and Fitzgerald³ have given conflicting results. However, whether pressure causes an increase or a decrease of temperature, in either case the shifts of the spectral lines may conceivably be due to a change in temperature rather than pressure, and experiments were undertaken to clear up this point. In accordance with Wilson and Gray's⁴ work, which indicates that the temperature of the negative pole is much less than that of the positive, a long arc, due to a fairly

¹ *Ap. J.*, March 1897.

³ *Ap. J.*, February, 1897.

² *Proc. R. Soc.*, May 30, 1895.

⁴ *Proc. R. Soc.*, November 24, 1894.

heavy current, was formed at right angles to the slit of the spectroscope, and one part of a photographic plate exposed to the spectrum due to the arc close to the positive and the other part to the spectrum as formed by the arc near the negative pole. No change, however, was detected in the position of the lines. Another method of testing the same point was to vary between wide limits the strength of current used, since the temperature, according to Moissan,¹ probably rises with increase of current. The extreme currents used were two amperes and 180 amperes respectively, but the positions of the lines appeared to remain absolutely unchanged. Further tests were made on the sodium line D_2 (one of the most sensitive of all lines examined) as produced first in the Bunsen flame and then in the electric arc; but while the temperatures of the vapor in the two cases were probably widely different the position of the line remained the same, as nearly as could be determined. Again one would certainly expect the outer envelope of an electric arc to be much cooler than the core, but the position of a reversal given by the former is exactly the same as that of a fine sharp line produced by the latter. The expression, "temperature of the arc or flame," is used with hesitation, since so little is known of the mean condition of the molecules producing light, but the negative results of all the above experiments give every assurance that the shifts of the lines are not ordinary temperature effects. It should be stated, however, that the luminous intensity of the arc greatly increased, especially where metallic poles were used, with increase of pressure.

The numerous negatives obtained, as well as the eye observations made, show that the general effect of pressure is to broaden the lines and to bring out their reversals. However, this is not always the case, since lines often appear quite as fine and sharp at one pressure as at another; and in all probability the broadening of the lines is due, chiefly at least, to an increase of density of the gas producing them, since it is always greater the greater the amount of the substance used in the arc. This

¹ *Annals de Chimie et de Physique*, October 1896, p. 231.

idea is also in accord with Schuster's¹ observation that when gases are mixed in different proportions the lines of any one become sharper when it is present in smaller quantity, though the total pressure may remain the same.

The lines of the cyanogen bands came out more strongly on my plates under pressure (the pressure being due to atmospheric air), but never showed much if any shift, which fact furnished conclusive evidence that the shifts of other lines were due to real changes in wave-frequencies and not to some disturbance of the apparatus, since they were all photographed simultaneously on the same plate, the lines of the cyanogen bands never being appreciably displaced while other lines were.

The shift or displacement of any line is directly proportional to the excess of pressure above one atmosphere (the position of the line as formed at atmospheric pressure being taken as its normal or zero position) and is always towards the less refrangible or red end of the spectrum. The same law has been shown by Mohler² to hold for pressures below one atmosphere—the shift in this case being to the violet. The shift is very different for the lines of different elements, and also, in many cases at least, for different groups of lines of the same element. In particular the shifts of the several series of lines (as given by the alkalis), principal and subordinate, are by no means equal, even when the lines are of approximately the same wave-length, as shown by the tabulated results in Table I. Lines of the second subordinate series seem to shift about twice as much as those of the first, which in turn are displaced to an extent approximately twice that of the lines of the principal series. A few iron lines, each of which is more hazy or softer than the average line of this element, are shifted about three times as much as other lines of the same substance. Again, all the nebulous or hazy copper lines examined shift to approximately the same extent (allowance being made for wave-length) but much more than do other lines of the same element. It is worth noting that these nebulous lines of copper were best obtained when both poles of the

¹ *Ency. Brit.*, "Spectroscopy."

² *Ap. J.*, October 1896.

arc were metallic rods, brass and copper or both copper, and that apparently the only effect of pressure on them was to greatly increase their wave-lengths. In this connection mention must be made of the calcium line *g*, which is shifted about twice as much as the similar calcium lines *H* and *K*. The same thing is also true of the three corresponding lines of strontium and of barium.

Similar lines of any given element, that is, lines belonging to the same series, or to no series but of the same character, shift to extents proportional to their wave-lengths. The most conclusive evidence of this proportionality was furnished by lines of different orders of spectra that appeared on the same plate. Thus ultra-violet lines of the third order were often found on the same plate with similar lines of the second of longer wave-length but due to the same element, and their measured shifts were approximately the same. Since the wave-length of a line of the third order is to that of one of the second that occurs at the same place as two to three, while the dispersion in the third order is to that in the second as three to two, it follows that constancy of measured shifts means that it is proportional to wave-length. For the sake, therefore, of comparison it seemed advisable to reduce the shifts of all lines to what they would be at some definite wave-length; the one chosen being 4000 Ångström units, since most of the work was done in that neighborhood.

It should be stated that in some cases the values obtained for the shifts of the lines may have been due in a measure to unsymmetrical broadening; but this has certainly not led to much error, since as already stated, only those lines were used which could be fairly accurately measured, that is, those which were either comparatively narrow or else reversed.

DESCRIPTION OF TABLE I.

The results of the numerous measurements are given in Table I, in which the upper numbers in the line of each wave-length are the observed shifts in thousandths of an Ångström unit, and the lower their values reduced to wave-length 4000. In many cases the observed shift, as given, is the average of fairly con-

cordant measurements of the same line on different plates. The different pressures used are given in atmospheres at the heads of the columns, and are greater by unity (since the lower pressure of each experiment was always one atmosphere) than the difference in pressure, $p - p_0$, to which the shift was actually due.

In most cases the wave-lengths are taken either from Professor Rowland's Table of Solar Spectrum Wave-lengths, in process of publication in the *ASTROPHYSICAL JOURNAL*, or from a former table of his published in *Astronomy and Astro-Physics*.¹ Some are taken from the papers of Kayser and Runge, and a few from other sources, but it was found necessary, for the want of suitable tables, to determine a number of them by comparison with known lines in their neighborhood, and since exact wave-lengths are not essential to this work, only such approximations of them are given as will serve to surely identify the lines in question.

TABLE I.

Showing the pressure in atmospheres and the observed resulting shifts ($\Delta\lambda$) in thousandths of an Ångström unit, and the same reduced to wave-length 4000.

ALUMINIUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000										
	4¼	4¾	6	7	7½	9	10½	10¾	11¾	12¾	14
3082.27 ..				38 50		38 50					
3092.84 ..				40 52		38 50					
3944.114..		17	29	29				44	49	48	68
3961.674..	17	25	26	37	36		44	45	50	49	69
							45	40	57	52	76
								41	58	53	77
Average.	17	21	28	38	36	38	44	42	53	50	72
				46	36	50	45	43	54	51	73

NOTE.—Several lines of the aluminium oxide band, 4842–5041, were measured on two plates which were taken at different pressures. The shift, if anything, was very small.

¹*A. and A.*, 12, 1893.

TABLE I.—Continued.

ANTIMONY.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
			6¾			
3267.6.....			21 26			

BARIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000						
	7	8	8½	10	10½	11	12
	45						78
4432.13.....	41						71
	36					56	69
4506.11.....	32			56	68	50	61
	32	52					80
5535.69.....	23	38		40	50		58
Group A.							
	38	52		56	68	56	76
Average	32	38		40	50	50	63
	23		24	32	34	40	
4554.211.....	20		21	28	30	35	
			23	34			
4934.237.....			19	28			
Group B.							
	23		24	33	34	40	
Average	20		20	28	30	35	
							117
3910.04.....							120
							119
3935.87.....							121
							126
3993.60.....							126
							135
4726.63.....							115
Group C.							
							124
Average							120

TABLE I.—*Continued.*

ARSENIC.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
		8½	9	10	
2745.09.....				20	
				29	
				22	
2780.30.....				32	
				20	
2860.54.....				28	
		20	18		
2898.83.....		28	25		
		20	18	21	
Average.....		28	25	30	

BERYLLIUM (GLUCINUM).

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
			7½		
3130.6.....			11		
			14		
			19		
3321.3.....			24		
			19		
3321.5.....			24		
			16		
Average.....			21		

BORON.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
	8	8½	9	9¼	
2496.867.....	19	23	23	25	
	30	37	37	40	
	18	18	22		
2497.821.....	30	30	35		
	19	21	23	25	
Average.....	30	34	36	40	

TABLE I.—*Continued.*

BISMUTH.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
			10	13½		
2898.08.....			26			
			35			
			34			
2989.15.....			45			
				48		
3397.31.....				57		
			30	48		
Average.....			40	57		

CÆSIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
			6	7		
			138	123		
4555.44.....			121	108		
			95	78		
4593.34.....			82	68		
			117	101		
Average.....			102	88		

CARBON.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
		8	8½	9	9½	10
		24	20	24	23	26
2478.661.....	38	32	38	38	42	

NOTE.—A number of "cyanogen" lines were measured at various pressures, and found to shift very little, if at all.

TABLE I.—Continued.

CADMIUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000						
	7	7½	8	9	9½	10	10½
3261.17					18 22		
3466.33					20 23		25 28
3610.66						20 22	
No series.							
Average					19 23	20 22	25 28
6438.680	Reduced to λ 4000 and for a pressure of 12 atmospheres $\Delta\lambda=80.1$						
3403.74					29 34		25 30
3467.76					27 31	18 21	20 23
3613.04					16 18	19 21	
First subordinate series.							
Average					24 28	19 21	23 27
3081.03	40 53			60 80			
3133.29	48 60			51 65			
3252.63		31 38			47 57	56 69	
4678.347				54 47	79 68		
4800.080			43 36	48 40	70 58		
5086.078	53 42	59 47	63 50	67 54	70 56		82 66
Second subordinate series.							
Average	47 52	45 43	53 43	56 57	67 60	56 69	82 66

¹ Mean of several concordant eye observations by different persons and at different pressures.

CALCIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000											
	3	4½	5	6	7	8	9	10	10½	11	12½	14½
K 3933.825									25	24	28	
H 3968.625									22	26	33	
4283.169			13	18		29				31	30	
4289.525			12	17		27				29	28	
4299.149	8	8	15	16		20				33	35	40
4302.692			17	13		22				33	32	34
4307.91			16	12		27				31	30	
4318.80				11		25				28	27	
Group A				27				24		30		
Average	8	8	15	17		25		22	24	28	31	33
3158.98						42	47					
3179.45						53	37					
g 4226.904						47	42					
4435.13 ¹						40		45		48		
4454.97 ¹										51	56	87
5588.985										48	53	82
5594.691										81		
5598.711										74		
5603.083										80		
Group B						66	68			73	70	
Average					47	66	49	80		50	72	
4425.61					47	68	57	74		52	63	
4435.86					49		55			47		
4456.08						56						
1st subordinate ser.						40						
Average												
6102.99	² 67		² 117			² 166	² 203					
6122.46	44		77	² 82		109	133					
6162.46	² 53					² 140				² 215		
	35		53			91	² 148			141	² 214	
		² 84					96			139		
2d subordinate ser.												
Average												
	² 67		² 117			² 166	² 203					
	44		77	² 82		109	133					
	² 53					² 140				² 215		
	35		53			91	² 148			141	² 214	
		² 84					96			139		

¹ (Occurs with lines of 1st subordinate series, and shifts to the same extent.

² Eye observations.

CERIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
		6½	8		
3895.224.....		20			
		21			
		14			
3896.917.....		14			
		22			
3898.4.....		23			
		17			
3912.5.....		17			
		13			
3917.7.....		13			
		8			
3918.4.....		8			
		20			
3919.9.....		20			
		22			
3921.6.....		22			
		17			
3929.3.....		17			
		17			
3931.2.....		17			
		19			
3940.4.....		19			
		8			
3941.1.....		8			
			8		
3949.2.....			8		
		8			
3953.7.....		8			
		10			
3955.4.....		10			
			15		
3957.4.....			15		
		7			
3961.0.....		7			
		6			
3964.6.....		6			
		12			
3971.8.....		12			
		17			
3972.2.....		17			
		19			
3975.1.....		19			
		7		9	
3978.7.....		7		9	
		12			
3984.7.....		12			
		11			
3989.5.....		11			
		15		21	
3992.5.....		15		21	
		17			
3993.0.....		17			
		14		13	
Average.....		14		13	
		14		13	

TABLE I.—Continued.

CHROMIUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000											
	4¾	6	7	9¾	10	10½	11	11½	12¼	12½	14	14½
3886.932..	4	4					26				36	
		16					27				37	
3919.309..							20			12	29	
	7						33				32	
3941.637..	7	7	12	16	25	23	34	27			33	
3963.831..	7	12	16	25		23	27			36	47	
3976.839..	14	12	12				28	28			38	
	12						34				49	
3984.059..	12						34				49	
4026.318..			19									
	3	9	19				26				26	30
4254.505..	3		18				24				24	28
					17							
4266.894..					16							
	14	11					31				40	31
4274.958..	13	10					29	30	22	24	38	29
4280.556..							28	22				
							34				41	
4289.885..							32				44	
Average	9	9	14	16	25	17	23	29	23	24	24	38
		13	15	25	16	23	28	22	22	24	37	29

COLUMBIUM (NIOBIUM).

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000					
			8½	9½		
3914.8.....				27		
				28		
3937.7.....				13		
				13		
4059.0.....			22	24		
			22	24		
4079.9.....			30	32		
			29	31		
				26	24	
Average			26	24		

TABLE I.—Continued.

COPPER.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000					
	7	8	$12\frac{1}{4}$	$12\frac{1}{2}$	13	$13\frac{1}{2}$
2883.03.....	11	8 10				
3010.92.....	15	11				
3036.17.....	12	9				
3073.89.....	10	7				
3094.07.....	17	13				
3247.680.....			25	28		28
3274.092.....			30	33		33
			20	32	30	36
			25	38	36	41
3317.28.....		13				
		16				
3337.095.....	13	11				
	8	13				
3476.07.....	10	14				
	12	16				
3483.82.....	14	17				
	16	19				
3520.07.....	18					
3524.31.....	12	19				
	14	21				
3533.84.....	13					
	15					
3545.05.....	17					
	19					
3599.20.....	15	17				
	17	19				
	10					
3621.33.....	11					
	16					
3636.01.....	18					
	13					
3684.75.....	15					
		20				
5105.75.....		16				
Lines of small shift. Several others of this set were measured						
Average	12	15	23	30	30	32
	14	16	28	36	36	37
	27	28				
3365.46.....	32	33				
	24					
3381.52.....	28					
	36					
3620.47.....	40					

TABLE I.—*Continued.*COPPER—*Continued.*

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
	7	8	12¼	12½	13	13½
3741.32.....	35 38					
3860.64.....	35 37					
5218.45.....		43				
Lines of medium shift		33				
Average	31 35	36 33				
4177.87.....	87 83					
4249.21.....	57 54					
4275.32.....	64 60					
4378.40.....	81 74					
4415.79.....	80 73					
4587.19.....	74 64					
5292.75.....		68 52				
Lines of large shift. Several others belong to this set. Most of these lines are "soft" and broad						
Average	74 68	68 52				
5153.33.....		27 21				
5220.25.....		30 23				
First subordinate series		29				
Average		22				
4480.58.....	50 44					
4531.04.....	53 46					
Second subordinate series		52				
Average	45					

TABLE I.—Continued.

COBALT.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
		$9\frac{3}{4}$	$11\frac{1}{4}$	$12\frac{1}{2}$	$14\frac{1}{2}$
3354.515.....				19 23	33 39
3361.413.....				18 22	
3395.016.....				20 24	22 26
3405.255.....		17 20			
3409.336.....		14 16			23 27
3417.384.....				23 27	29 34
3461.326.....		18 21			
4121.476.....			20 19		
Average		16 19	20 19	20 24	27 32

ERBIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
				8	
3988.....				30 30	

GERMANIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
			7	$8\frac{1}{2}$	9
3039.198.....				22 29	24 31
3269.628.....				24 29	22 27
4226.724.....			30 28		
Average			30 28	23 29	23 29

TABLE I.—Continued.

GOLD.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
			7	10	10½	
3122.88.....					20 26	
3898.04.....					40 41	
3909.54.....					25 26	
4041.07.....			20	25		
4065.22.....			34 33	34 33		
Average.....			27 27	30 29	26 29	

INDIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000						
	7	9½	10	10½	11½	12½	14½
3256.17.....		19 23	23 28				
No series		36	37				
3258.66.....		44	45				
1st subordinate series							
2932.71.....	60	43			69		
4102.00.....					68		
4511.345.....		73	83	81		102	125
2d subordinate series		65	74	72		90	111
Average.....	60	43 65	73 74	83 72	81 68	69 90	102 111

IRON.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000													
	4¾	6	7	9	10	11	11¼	11½	12¼	12½	12¾	13	14	14½
3997.547 ...							29							
4005.408 ...			15		23	32								
4009.864 ...					18									
4045.975 ...	8	9					20	20						
4063.759 ...							23							
4181.919 ...					25									
4199.267 ...					24									
4207.291 ...					17									
4219.516 ...					18									
4236.112 ...	8		17		17		26							
4250.945 ...			16		25		31			35	25		34	
4271.934 ...	8	13	11		26					23	24		32	
4294.301 ...			14		25		28	20	28	23	26		30	30
4298.195 ...					23		26	19	26	22	24		28	28
4325.939 ...					26									
4377.948 ...					24									
4382.928 ...					24									
4383.720 ...														
4404.927 ...														
Many other lines belong to this group														
Average..	8	11	14		23	29	25	23	27	29	28	35	32	31
4222.382 ...									70					
4227.606 ...									77					
4233.772 ...									73					
4236.112 ...			26	59	60				75					
4250.287 ...			57	95	84	81			75					
4260.647 ...			54	90	80	77			74			81		
4271.934 ...			47	72	66	69			74			81		
			45	68	63	65			70			81		
			59	98	74	82			84					
			56	92	70	77			79					
Average..			47	81	71	77			77			86		
			45	76	68	73			73			81		

NOTE.—Other lines, among them 5569.77, 5573.05, and 5586.92, belong to this group.

TABLE I.—*Continued.*

LANTHANUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000	
	8	9
3921.695.....		21
		21
	13	32
3929.363.....	13	33
	26	24
3949.199.....	26	24
	21	35
3995.899.....	21	35
	7	14
4031.865.....	7	14
	29	
4043.054.....	29	
	17	
4077.498.....	17	
	21	
4086.861.....	21	
	19	25
Average.....	19	25

LEAD.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000			
	9	11	11½	13½
3639.728.....				63
				70
				70
3683.622.....				76
	49	55	49	
4058.041.....	48	54	48	
	49	55	49	67
Average.....	48	54	48	73

LITHIUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000													
	2½	3	4	4½	5	5½	6	6½	7	8	9	9½	10	10½
6708.2	¹ 18 11	¹ 24 14	¹ 30 18				¹ 66 40		¹ 52 31					¹ 130 78
3232.77										66	53 74			
Principal series														
6103.77	¹ 38 25	¹ 37 24		¹ 56 37		¹ 77 50		¹ 116 76				¹ 177 116		
1st subordinate series														
4972.11										222 181				
2d subordinate series														

¹ Eye observation.

MANGANESE.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000									
	4¾	6	7	10½	11	11¼	11½	12½	12¾	14
4018.269 . . .		¹ 3 8	¹ 2 12					¹ 2 32	¹ 2 27	¹ 3 37
4026.583 . . .	8				¹ 7 17					
4030.947 . . .		8	¹ 8 18	¹ 3 13		¹ 9 19			¹ 3 33	¹ 4 34
4035.883 . . .	8	¹ 8 18	¹ 3 13						¹ 2 26	¹ 2 32
4061.881 . . .						¹ 0 20				
4235.298 . . .	¹ 0 10		¹ 2 22							
4235.450 . . .	8	¹ 8 8	¹ 7 17	¹ 5 25	¹ 4 34	¹ 7 37			¹ 2 32	¹ 6 36
4239.890 . . .	¹ 2 12	¹ 3 20	¹ 2 21				¹ 9 29	¹ 1 31	¹ 4 45	¹ 7 47
4257.815 . . .	¹ 3 13	¹ 4 20	¹ 2 21	¹ 3 23	¹ 6 36	¹ 9 39			¹ 3 43	¹ 7 47
4266.081 . . .	¹ 3 13	¹ 4 20	¹ 9 20	¹ 2 22	¹ 3 38		¹ 7 37	¹ 4 40	¹ 3 41	¹ 6 46
4281.257 . . .	9	¹ 0 10	¹ 2 21	¹ 3 35	¹ 7 37	¹ 3 43	¹ 6 36	¹ 9 39	¹ 3 38	¹ 4 44
4284.223 . . .	¹ 1 11	¹ 2 12	¹ 0 20	¹ 4 34	¹ 0 40		¹ 6 36	¹ 8 38	¹ 5 35	¹ 1 41
Average .	¹ 0 10	¹ 1 18	¹ 9 19	¹ 8 18	¹ 3 30	¹ 2 32	¹ 0 20	¹ 7 34	¹ 0 38	¹ 0 40

MAGNESIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000						
	7½	8	8½	9	10	11	13
2795.632.....			8 12	19 27			
2802.805.....			18 26	16 23			
2852.239.....	12	6			23	21	29
No series	17	9			32	30	37
Average.....	12	6	13	18	23	21	29
	17	9	19	25	32	30	37
3829.501.....				33 34	28 29		
3832.450.....				30 31	31 32		
3838.435.....				40 41	30 31		
1st subordinate series							
Average.....				34 35	30 31		
5167.497.....				66 51			
5172.856.....				62 48			
5183.791.....				47 36			
2d subordinate series							
Average....				58 45			

* This line, much the strongest in the spectrum of magnesium, is nearly coincident with, and consequently almost always obscures a much weaker line of the first subordinate series.

MERCURY.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
		10	11		
3650.3.....		63 70	63 70		
5461.0.....		90 66			
Average.....		77 68	63 70		

TABLE I.—*Continued.*

MOLYBDENUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000	
	9	11½
3132.749.....		31 40 27
3158.3.....		34 28 32
3170.5.....	33	40 18 33
3194.2.....	22	41
Average.....	28	23 39 31

NICKEL.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000		
	9¾	12½	14½
3391.180.....		14 17 19	
3413.637.....		23	19
3414.092.....		23	
3437.447.....	20 23	34 27 31	39 29 33
3458.606.....		16 18 25	23 24 35
3461.322.....		27	40
3500.993.....		34	41
3515.207.....		38	45
3524.677.....		30	
5155.937.....	24 18	35	
Average.....	20 20	24 26	35 39

TABLE I.—*Continued.*

NEODYMIUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000	
		9
4279.874.....	17	18
4281.0.....	7	7
4284.8.....	6	6
4302.7.....	7	7
4319.1.....	11	12
4334.3.....	5	5
4348.0.....	10	11
4362.2.....	5	5
4385.8.....	14	15
4401.0.....	13	14
4420.7.....	5	6
And many others		
Average.....	9	10

OSMIUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000	
	12 $\frac{3}{4}$	13
4260.993.....		17
4520.633.....	18	16
	20	18
Average.....	18	16

PALLADIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
		12	13½		
3373.139.....			33		
			39		
			40		
3404.725.....			47		
		17	38		
3421.367.....		20	44		
			31		
3433.578.....			36		
			31		
3441.539.....			36		
		18	27		
3460.884.....		21	31		
		21	25		
3481.300.....		24	29		
		19	30		
3489.915.....		22	34		
		22	44		
3609.696.....		24	48		
			41		
3634.841.....			45		
		17	28		
3690.483.....		19	31		
		19	33		
Average		22	38		

PLATINUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
		12¼	12¾	13	14¼
2830.41.....				16	
				22	
				14	
2893.98.....				20	
				12	
2897.99.....				17	
			12	17	
2929.91.....			16	24	
		15	17	18	13
2998.079.....		20	23	25	18
				18	23
3042.745.....				25	31
					16
3064.824.....					21
		25		31	
4442.723.....		23		28	
		20	15	18	18
Average		21	20	23	24

TABLE I.—Continued.

POTASSIUM.*

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
		8	9		
4044.294		76	93		
		75	92		
4047.338		88	106		
		87	105		
Principal series					
		82	99		
Average		81	98		

RHODIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
	12	12¼	12¾	13	14½
3399.839	17				
	20				
	23				
3412.417	27				
	16				
3435.039	19				
	19				
3462.184	21				
	20				
3474.920	23				
	22				
3479.053	25				
	21				
3502.674	24				
	26				
3507.466	29				
	16				
3626.744	18				
	15				
3658.135	17				
	23				
3666.366	25				
	27				
3690.853	29				
				45	
4211.304				43	
		31	38	45	37
4374.981		28	34	41	34
	20	31	38	45	37
Average	23	28	34	42	34

TABLE I.—*Continued.*

RUBIDIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000			
		8	$8\frac{1}{2}$	
4201.98.....		70	73 123 117	
4215.72.....		71	75 88 84	
Average		71	74 106 101	

RUTHENIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000			
			12	
3429.689.....			29 34	
3499.095.....			26 30	
3593.178.....			21 23	
3599.914.....			27 30	
3625.330.....			32 36	
3635.084.....			20 22	
3637.612.....			25 28	
3661.525.....			33 36	
3663.520.....			17 19	
3669.688.....			23 25	
3678.456.....			20 22	
3727.073.....			25 27	
3728.173.....			21 23	
3730.577.....			33 36	
Average			25 28	

TABLE I.—Continued.

SCANDIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
				12		
4247.0.....				22		
				21		
4314.3.....				30		
				28		
4320.9.....				26		
				24		
				26		
Average.....				24		

SILICON.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000						
	$8\frac{1}{2}$	9	$9\frac{1}{2}$	10	11	$11\frac{1}{2}$	12
	13						
2506.994.....	21						
	12						
2516.210.....	19						
	18						
2519.297.....	28						
	13						
2524.206.....	21						
	22						
2528.599.....	34						
	20	21		25	31		
2881.695.....	28	29		35	40		
			31		44	40	39
3905.660.....			32		45	41	40
	16	21	31	25	38	40	39
Average.....	25	29	32	35	43	41	40

TABLE I.—*Continued.*

SILVER.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000				
	8	9½	12½	13	
3280.80.....	29 34	28 33	32 39		
3383.00.....		34 40	27 32	32 38	
Average	29 34	31 37	30 36	32 38	

SODIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000								
	3	3½	6½	7	7½	8	8½	9	10½
3302.504.....						47 57	67 81		
3303.119.....						61 74	57 70		
D ₂ 5890.182.....	¹ 30 20		¹ 69 47	62 42				94 62	¹ 121 82
D ₁ 5896.154.....		¹ 25 17	¹ 63 43	78 53				122 83	¹ 116 79
Principal series...									
Average	30 20	25 17	66 45	70 48		54 66	62 76	108 73	119 81
5682.861.....					314 221	¹ 400 280		426 300	
5688.434.....	¹ 100 70	¹ 130 91			368 259	¹ 345 242		460 323	
2d subordinate series									
Average	100 70	130 91			341 240	373 261		443 312	

¹ Eye observation.

TABLE I.—Continued.

STRONTIUM.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000					
	$8\frac{1}{2}$	10	$10\frac{1}{2}$	11	$11\frac{1}{2}$	12
4077.885.....				26	39	
4215.703.....	28		34	26	38	
4742.07.....	27		32	34	45	
4784.43.....				32	43	
4812.01.....				42	37	
4832.23.....				36	31	
4876.35.....				42	35	
5222.43.....				35	29	
5225.35.....				23		29
5229.52.....				19		24
5238.76.....				50	48	
5257.12.....				41	40	
Group A.....				40	40	
Average.....				33	33	
3351.35.....			46			
3380.89.....			35			
3464.58.....			60			
4607.510.....			46			
4962.45.....			57			
Group B.....			34			
Average.....			45			
3351.35.....			34			
3380.89.....			60			
3464.58.....			46			
4607.510.....			57			
4962.45.....			34			
Group B.....			45			
Average.....			34			
3351.35.....			60			
3380.89.....			46			
3464.58.....			57			
4607.510.....			34			
4962.45.....			45			
Group B.....			34			
Average.....			45			

TABLE I.—Continued.

TANTALUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000			
			12	
3918.6.....			13	
			13	
			19	
3922.9.....			19	
			11	
3931.1.....			11	
			16	
3970.3.....			16	
			18	
3982.1.....			18	
			23	
3988.9.....			23	
			14	
4003.9.....			14	
			14	
4007.0.....			14	
			18	
4027.1.....			18	
			21	
4030.1.....			21	
			15	
4061.6.....			15	
			20	
4064.8.....			20	
			18	
4105.2.....			18	
			17	
Average			17	

THALLIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000			
		9½	11	
3519.342.....		49	¹ 87	
	56		99	
3529.58.....			¹ 75	
			86	
Average		49	81	
	56		93	

¹ Good lines.

TABLE I.—*Continued.*

TUNGSTEN.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000			
		$9\frac{1}{2}$	11	
4009.0.....		20	13	
4074.7.....		20	15	
Average.....		20	14	

TIN.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000				
	$9\frac{3}{4}$	10	$12\frac{1}{2}$	13	$14\frac{1}{2}$
2706.61.....		20			
2812.70.....		30			
2840.00.....		40			
2850.72.....		57			
2863.41.....		24			
3009.24.....		34			
3032.88.....		24			
3034.21.....		34			
3175.12.....		35			
3262.44.....		25			
3330.71.....		31			
Average.....		41			
		22			
		30			
		36			
		48			
			48		54
			59		68
	37		47	44	51
	46		58	55	63
			44		64
			55		77
	37	28	48	44	58
	46	39	58	55	69

TITANIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
	8	8½	9	10½	11	11½
	20					
3186.564.....	25	22	21			
3192.120.....	27	18	26			
3200.034.....	22	15	31			
3222.970.....	19	12				21
3234.635.....	15	13				26
3236.703.....	16	13				18
3239.170.....	16	12				22
3242.125.....	15					27
3254.314.....		17				15
326.907.....		21	14			18
3341.067.....	18	15	15			19
3349.043.....				14		23
3361.327.....		8	9	16		17
3372.901.....		10	16	18		20
3380.397.....		19	17			
3900.681.....		17	15			
3904.926.....		15	15			
3913.609.....		15	13			
3924.673.....		13	9			
3930.022.....		9	10			
3947.918.....		10	9	19		
3948.818.....		9	11	13		18
3956.476.....		11	13	16		18
3958.355.....			16	18		
3981.917.....			18	15		16
3989.912.....			15			16
3998.790.....					15	22
4009.079.....		13				
4024.726.....		13	15			
Average.....	19	16	14	16	14	15
		15	16	17	15	21

THORIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000					
			8	9		
4248.1.....			12 11	15 14		
4283.7.....			14 13			
4381.6.....			7			
4391.3.....			9 8	8 7		
4433.2.....			14 13	11 10		
4439.3.....			15			
4441.1.....			14 15	20 18		
4465.5.....			21 19	12 11		
4487.7.....			4 21			
4510.7.....			19			
Average.....			13 12	13 12		

YTTRIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000							
	4¾	6	7	10	11	12½	13	
3950.497.....	5 5 4	7 7			15 15	17 17 17	14 14 18	
3982.742.....	4		4					
4309.780.....				11 10				
4358.892.....				17 16 21				
4375.110.....				19 23				
4398.185.....				21 20				
4422.760.....				18				
Average.....	5 5	7 7	4 4	18 17	15 15	17 17	16 16	

NOTE.—Several other yttrium lines were measured, and found to agree well with the above.

VANADIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000	
	8	10
	5	
3902.399.....	5	13
3910.984.....	9	13
3913.0.....	14	17
3914.5.....	14	23
3922.560.....	13	24
3924.8.....	13	22
3925.4.....	22	18
3928.1.....	12	18
3934.2.....	12	14
3937.7.....	14	5
3938.3.....	5	19
3939.5.....	18	19
3950.4.....	20	20
3950.6.....	26	23
3979.6.....	26	23
3984.5.....	15	15
3984.7.....	17	17
3989.0.....	17	15
3990.712.....	16	15
3992.971.....	21	24
3998.9.....	21	24
4042.8.....	12	22
4051.204.....	12	22
4051.491.....	22	15
4057.2.....	15	14
4092.821.....	14	17
4105.318.....	17	16
4120.6.....	16	19
4123.539.....	19	24
4128.251.....	24	10
4132.100.....	10	23
4134.589.....	23	17
Average.....	17	18
	17	19
	18	13
	21	22
	16	19
	16	19

TABLE I.—*Continued.*

URANIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000			
		$9\frac{1}{2}$	11	12
3886.4.....				12
3993.6.....		4	3	
3912.7.....			5	
3916.0.....			4	
3932.2.....		7	11	14
3951.5.....			7	
3954.9.....			6	
3982.6.....			4	
3986.0.....			5	
3987.6.....			13	
3989.7.....			12	
4050.3.....			10	
4064.6.....			13	
Average.....		6	8	13

ZIRCONIUM.

Wave-length λ	$\Delta\lambda$ observed and Pressure in atmospheres, followed by $\Delta\lambda$ reduced to λ 4000			
			9	
3958.355.....			13	
3999.117.....			24	
4029.796.....			23	
Average.....			20	

TABLE I.—*Continued.*

ZINC.

Wave-length λ	Pressure in atmospheres, followed by $\Delta\lambda$ observed and $\Delta\lambda$ reduced to λ 4000					
	7	8	9¾	11½	12¼	13½
	12					
3075.99.....	16	30		31		
3302.67.....		36		37		
		26		32		
3345.13.....		30		38		
		30				
3346.04.....		36				
No series						
	12	29		32		
Average.....	16	34		38		
		27		32		
3282.42.....		33		39		
		22		37		
3303.03.....		27		44		
		25		33		
3345.62.....		30		39		
1st subordinate series						
		25		34		
Average.....		30		41		
		46				
3018.50.....		62				
		44				
3035.93.....		58				
		49				
3072.19.....		64				
		61	68	60		
4680.317.....		52	58	51		
		51	62	77	58	63
4722.341.....		43	52	63	49	53
		56		68	67	74
4810.724.....		47		57	56	62
2d subordinate series						
		51	65	68	63	69
Average.....		54	55	57	53	58

RELATIONS OF THE SHIFTS TO EACH OTHER AND TO CERTAIN
PROPERTIES OF THE ELEMENTS

As already stated, at least many elements produce lines whose shifts for the same wave-length are quite different, but this difference is by no means a haphazard one. Thus any series (as described by Kayser and Runge) of lines produced by an element gives shifts which, when reduced to the same wave-length, are approximately equal, while the shifts of the series, principal, first and second subordinate, are to each other respectively very nearly as 1 : 2 : 4. As is well known, the lines of any series of a given element are quite similar in general appearance, but very different from those of other series; and the same is true of the several groups of lines, of iron and of copper, for instance, which have such different shifts. In general, then, it appears that lines of the same character of any element, when reduced to the same wave-length, give equal shifts, which, nevertheless, may differ widely from those of a different character, though of the same element.

Lines of the same series, not only of a given element, but also those of different elements, resemble each other closely, and consequently in comparing shifts of lines with other properties of the elements, it is necessary to confine one's attention, as far as possible, to lines of the same character; and in accordance with this notion the following relations have to do with the shifts of what might be termed the most characteristic lines of the elements, that is, those lines which are the easiest to obtain (at least in the arc spectra) and which produce the sharpest reversals and consequently admit of the most accurate measurements.

On forming, for various elements, the product of the cube root of the atomic volume (*i. e.*, quotient of atomic weight divided by density) and the coefficient of linear expansion of the substance in the solid form, certain numbers are obtained whose ratios are approximately those of the shifts of the lines of the respective elements. This is shown in Table II, in which the atomic volume and coefficient of expansion both refer to 40° C.

TABLE II.

Element	Atomic weight W	$\rho \bar{W}$	Atomic volume V	Coefficient of linear expansion α	Temperature of melting point T	$\frac{48600}{T}$	Shift S	$\alpha \rho \bar{V}$
Al	27.11	3.00	10.6	2313	1123	43.3	55	50.6
Sb	120.43	4.94	17.9	1692 } 0882 }	710	68	49	{ 43 23
As	75.01	4.22	13.2	0559	>773	<63	39	13
Ba	137.43	5.16	36.5	?	748	65	58 } 34 }	?
Be	9.08	2.09	4.9	?	>1270	<39	36	?
Bi	208.11	5.93	21.1	1621	538	90.3	49	44.7
B	10.95	2.22	4	?	?	?	49	?
Cd	111.95	4.82	12.9	3069	593	82	76	75.6
Cs	132.89	5.10	70.6	?	?	?	161	?
Ca	40.07	3.42	25.4	?	>Sr	<Sr	54 } 27 }	?
C	12.01	2.29	3.6	0786 } 0540 } 0118 }	?	?	50 } 0 }	?
Ce	140.20	5.20	21	?	<1273	>38	27	?
Cr	52.14	3.74	7.7	?	?	?	26	?
Co	58.93	3.89	6.9	1236	2070	24	24	23.6
Cb	93.73	4.54	13.0	?	?	?	33	?
Cu	63.60	3.99	7.1	1678	1330	36.5	33	32.5
E	166.32	5.51	?	?	?	?	47	?
Ge	72.48	4.17	13.2	?	?	?	44	?
Au	197.23	5.82	10.1	1443	1310	37	40	67
In	113.85	4.85	15.3	4170	449	108.3	88	103.5
Fe	56.02	3.83	7.2	1210	2080	23.3	25	23.3
La	138.64	5.18	22.5	?	>710	<69	32	?
Pb	206.92	5.92	18.1	29.24	605	80.3	60	76.9
Li	7.03	1.92	12.9	?	453	107	85	?
Mg	24.28	2.90	13.9	2694	1023	47	62 } 44 }	65
Mn	54.99	3.80	6.9	?	2170	22.9	33	?
Hg	200.00	5.85	14.1	6000	233	209	81	145
Mo	95.99	4.58	11.1	?	?	?	40	?
Ndi	140.80	5.20	?	?	?	?	11	?
Ni	58.69	3.89	6.7	1279	1870	26.5	28	24
Os	190.99	5.76	8.5	0657	2770	17.5	17	13.4
Pd	106.36	4.74	9.2	1176	1775	27.4	27	24.7
Pt	194.89	5.80	9.1	0899	2050	23.7	20	18.5
K	39.11	3.39	45.4	8415	335	145	132	300
Rh	103.01	4.69	8.6	0850	2270	21.4	25	17.4
Rb	85.43	4.40	56.1	?	311	156	132	?
Ru	101.68	4.67	8.4	0963	2070	23.5	28	20
Sc	44.12	3.53	17 (?)	?	?	?	24	?
Si	28.40	3.05	11.4	0763	?	?	43	17
Ag	107.92	4.76	10.2	1921	1230	39.5	39	42.2
Na	23.05	2.85	23.7	7105	369	132	108	204
Sr	87.61	4.44	34.9	?	>Ba	<Ba	70 } 35 }	?
Ta	182.84	5.68	16.9	?	?	?	17	?
Tl	204.15	5.89	17.2	3021	563	86.3	102	78
Th	232.63	6.15	20.9	?	?	?	18	?
Sn	119.05	4.92	16.3	2234	503	96.6	55	50.6
Ti	48.15	3.64	13 (?)	?	?	?	22	?
W	184.83	5.70	9.6	?	?	?	19	?
U	239.59	6.21	12.6	?	?	?	11	?
V	51.38	3.72	9.3	?	?	?	25	?
Y	89.02	4.47	?	?	?	?	15	?
Zn	65.41	4.03	9.1	2918	676	71.9	57	61.2
Zr	90.40	4.49	21.7	?	?	?	28	?

and the shift to a pressure of twelve atmospheres and wave-length 4000.

A similar expression is used by Raoul Pictet in his formula for deducing the melting points of the metals. He finds that the continued product of the absolute melting point, the coefficient of linear expansion of the substance in the solid state and the cube root of the atomic volume is nearly the same for all metallic elements except antimony and bismuth. Table II also shows the relation between Pictet's results and the shifts of the lines by giving the quotients obtained by dividing a constant, namely 48600, by the absolute melting points of the elements. The number 48600 was chosen to reduce his results to numbers comparable with the shifts at twelve atmospheres, that of iron being made to coincide with the value given by the product of its coefficient of linear expansion by the cube root of its atomic volume. It appears that the shifts are about as near the calculated values as are the melting points, and consequently in most cases the product of the shift by the absolute melting point is nearly constant; or what amounts to the same thing, the shift is inversely proportional to the absolute temperature of the melting point.

DESCRIPTION OF TABLE II.

The first column gives the symbols of those elements some of whose lines have been examined. Under W are their atomic weights, and in the next column, marked $\sqrt[3]{W}$ the cube roots of these weights. Under V are the atomic volumes at 40°C. and under α the coefficients of linear expansion at the same temperature. The column marked T gives the absolute temperatures of the melting points, and that marked $\frac{48600}{T}$ the quotients indicated. Under S are the shifts at twelve atmospheres and wave-length 4000, and the last column, marked $\alpha\sqrt[3]{V}$, gives the product of the coefficient of linear expansion and cube root of atomic volume multiplied by 10^6 . The atomic weights are based on the assumption that the atomic weight of oxygen is 16, and are taken from a special Smithsonian publication (*Constants of Nature*, Part

V, Clark) for 1897. The atomic volumes and melting points are taken from Nernst's *Theoretical Chemistry*, and the coefficients of expansion from the *Physikalisch-Chem. Tabellen von Landolt und Börnstein*.

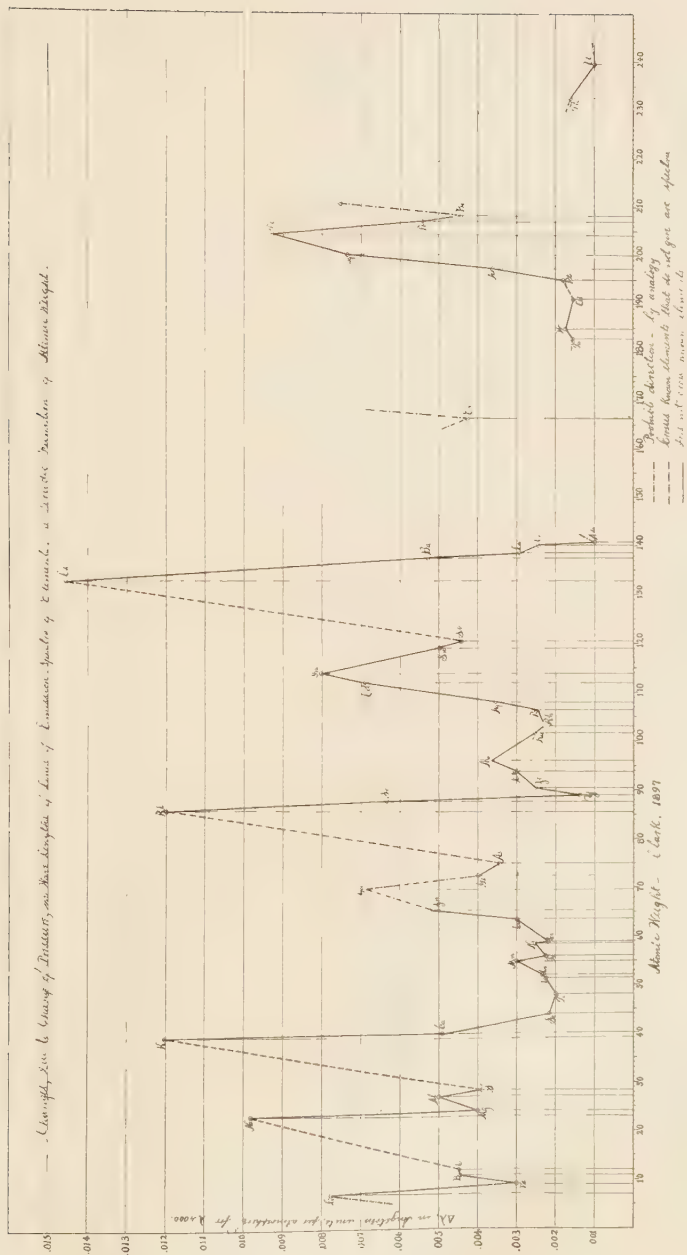
In a few cases, more recent and possibly more accurate values of the above constants have been obtained, but the differences are not sufficient to materially affect the calculated shifts.

Like many other properties of the elements, the shift of their spectral lines is a periodic function of atomic weight, as is evident from the line of shifts as plotted in Plate XVIII, in which the abscissæ are atomic weights and the ordinates the shifts per atmosphere of the lines of the given elements. The maxima fall, as do those of atomic volume, on the alkali metals, lithium, sodium, potassium, rubidium, and cæsium. In the case of those elements that have two or more groups of lines of different shifts, the group giving the best lines was always the one selected. Thus for the alkalies the lines selected are those of the principal series, which are by far the best lines for measurement of these elements, and besides, by selecting lines of the same series, it is possible to compare the shifts of the lines of the alkali metals, all of which belong to the same family of elements, or Mendelejeff group. For similar reasons lines of the second subordinate series were selected in the case of zinc, cadmium, and mercury. For calcium the *g* group of lines was selected, and the corresponding groups for strontium and barium. A different selection of lines where possible would not alter the periodic nature of the curve, but simply increase or decrease the values of the maxima and minima.

As shown by the results tabulated in Table II, those elements, such as sodium, potassium, indium, thallium, cadmium, and others, which have very large coefficients of linear expansion, have also very large shifts, and the converse is equally true.

Another and rather simple relation is this: The shifts of the spectral lines of similar elements, in the main those of the right or left half, as commonly tabulated, of a Mendelejeff group, are

PLATE XVIII.



PRESSURE SHIFTS OF SPECTRAL LINES AS A PERIODIC FUNCTION OF ATOMIC WEIGHT.

generally proportional to the cube roots of the atomic weights of the elements that produce them. This is shown in Table III, in which it will be seen that the observed and calculated values agree quite closely except in very few cases. The single carbon line shifts about twice the calculated amount, and the lines of a few other elements—platinum, osmium, yttrium, thorium, tantalum, and tungsten—only about half as much as would be expected. It is just possible that in these cases lines comparable to those measured of the other elements have not been selected. The lines measured of neodymium and uranium shift much less than the calculated amounts. Whether this is true of all the numerous lines of these two elements I am unable to state.

DESCRIPTION OF TABLE III.

Each horizontal row of Table III contains first the symbol of a certain element, followed by the observed shifts of its lines in thousandths of an Ångström unit for twelve atmospheres and wave-length 4000; then the symbol of an element of the same group followed by the calculated shift of its lines, and finally the observed shift of the same lines. The shifts marked *standard* are assumed to be correct, and each marked *calculated* deduced from the standard of the same horizontal row on the assumption that they are to each other as the cube roots of the atomic weights of the respective elements.

In determining the groups of similar elements I have been guided in some measure by their spectra, and since the grouping adopted is not exactly, though very nearly, that which is commonly made, I have thought it necessary to give it in Table IV. It will be seen that sodium, for instance, is classed with lithium, potassium, rubidium, and cæsium, which it strongly resembles spectroscopically, rather than, as is often done, with copper, silver, and gold, which it does not resemble in this respect. Again, and for similar reasons, magnesium is classed with calcium, strontium, and barium, rather than with zinc, cadmium, and mercury. In no case, however, is there a change of an element

TABLE III.

Showing shifts in thousandths of an Ångström unit for twelve atmospheres and wave-length 4000.

Standard		Calculated		Observed
Cs	161	Li	60	85
Cs	161	Na	90	108
Cs	161	K	109	132
Cs	161	Rb	139	132
Cu	33	Ag	39	39
Cu	33	Au	48	40
Ca	54 }	Mg	46 }	44 }
	27 }		23 }	30 }
Ca	54 }	Sr	70 }	65 }
	27 }		35 }	37 }
Ca	54 }	Ba	81 }	58 }
	27 }		40 }	34 }
Zn	57	Be	30	36
Zn	57	Cd	68	76
Zn	57	Hg	83	81
La	32	Y	28	15
La	32	Sc	22	24
Al	55	B	40	49
Al	55	In	89	88
Al	55	Tl	106	102
Ti	22	Zr	26	28
Ti	22	Ce	30	27
Ti	22	Th	35	18
Sn	55	C	26	50
Sn	55	Si	34	43
Sn	55	Ge	47	44
Sn	55	Pb	66	60
V	25	Cb	28	34
V	25	Ndi	35	11
V	25	Ta	38	17
Bi	49	As	35	38
Bi	49	Sb	41	49
Bi	49	E	45	47
Cr	26	Mo	32	40
Cr	26	W	40	19
Cr	26	U	43	9
Fe	25	Ru	36	28
Fe	25	Os	38	17
Ni	28	Pd	34	27
Ni	28	Pt	42	20
Co	24	Rh	29	25

from one to another of the Mendelejeff groups, and besides the right and left halves, as usually tabulated, are in the main retained, the only changes being in the case of elements of small atomic weights, which have many properties in common with the

elements of each half of their several groups, and which are often regarded as common to the two halves. Thus, as just stated, magnesium is placed with calcium, strontium, and barium, because spectroscopically it resembles them rather than zinc, cadmium, and mercury, though it has so many properties in common on the one hand with those of calcium, strontium, and barium, and on the other with those of zinc, cadmium, and mercury, that it might very well be classed with either group.

TABLE IV.

Showing the adopted grouping of similar elements.

Group I		Group II		Group III		Group IV		Group V		Group VI		Group VIII		
Li	Cu	Mg	Be	Sc	B	Ti	C	V	As	Cr		Fe	Ni	Co
Na	Ag	Ca	Zn	Y	Al	Zr	Si	Cb	Sb	Mo		Ru	Pd	Rh
K	Au	Sr	Cd	La	Ga	Ce	Ge	Ndi	E	W		Os	Pt	Ir
Rb		Ba	Hg		In	Th	Sn	Ta	Bi	U				
Cs					Tl		Pb							

SUMMARY OF RESULTS.

The following list of relations between the shifts of spectral lines, the conditions under which they are produced and the properties of the elements producing them is probably quite imperfect; some of them may be more or less accidental, and in all probability others quite as important have been overlooked. However, I have not searched at all carefully for such relations, and the present list contains only those which presented themselves from time to time during the investigation, and which I trust may be of service to anyone who attempts an explanation of the observed phenomena.

These relations are:

1. Increase of pressure causes all isolated lines to shift towards the red end of the spectrum.
2. This shift is directly proportional to the increase of pressure.
3. It does not depend upon the partial pressure of the gas or vapor producing the lines, but upon the total pressure.

4. The shift of the lines seems to be nearly or quite independent of temperature.

5. The lines of bands (at least of certain "cyanogen" and aluminium oxide bands) are not appreciably shifted.

6. The shifts of similar lines of a given element are proportional to the wave-lengths of the lines themselves.

7. Different series of lines (as described by Kayser and Runge) of a given element are shifted to different extents. When reduced to the same wave-length these shifts are to each other approximately as 1:2:4, respectively, for the principal, first and second subordinate series.

8. Similar lines of an element, though not belonging to a recognized series, are shifted equally (when reduced to the same wave-length), but to a different extent than are those unlike them.

9. Shifts of similar lines of different substances are to each other, in most cases, inversely as the absolute temperatures of the melting points of the elements that produce them.

10. The shifts of similar lines of different elements are to each other approximately as the products of the coefficients of linear expansion and cube roots of the atomic volumes of the respective elements (in the solid state) to which they are due.

11. Analogous or similar lines of elements belonging to the same half of a Mendelejeff group shift proportionately to the cube roots of their respective atomic weights.

12. The lines of those substances which, in the solid form, have the greatest coefficients of linear expansion have the greatest shifts. The converse is also true.

13. The shift of similar lines is a periodic function of atomic weight, and consequently may be compared with any other property of the elements which itself is a periodic function of their atomic weights.

The results of this investigation can be fairly well expressed by the simple equation.

$$\Delta \lambda = \alpha \beta \lambda (p - p_0)$$

when $\Delta \lambda$ is the increase of wave-length λ of any given line produced by the increase of pressure $p - p_0$, β a constant for any

series of lines and α a constant for any element. That is β for any series of a given element is the same as β for the corresponding series of any other element, while α for any series of a given element is the same as for α for any other series of the same element. If we write β_0 for the principal series, β_1 for the first subordinate and β_2 for the second subordinate, then, approximately, $\beta_0 : \beta_1 : \beta_2 = 1 : 2 : 4$.

By suitably choosing β , α may be replaced in most cases by $\frac{1}{T}$, where T is the absolute temperature of the melting point, or again by $\epsilon \sqrt[3]{V}$ where ϵ is the coefficient of linear expansion of the substance in the solid state and V the atomic volume (the objection to these expressions comes from the fact that for many elements neither T nor ϵ is known); or finally, for either half of any Mendelejeff group, by $\sqrt[3]{W}$, where W is the atomic weight. From this last expression it is evident that α , and therefore $\Delta\lambda$, is a periodic function of atomic weight.

The observations upon which the above conclusions are based, though very numerous, are by no means as complete as could be desired, and I feel quite sure that a more searching examination of a larger number of lines, probably at considerably increased pressures, would add materially to our knowledge of the interesting relations between the spectral lines and the conditions under which they are produced.

DISCUSSION OF THE RESULTS.

How to interpret the shifts of the lines, their relations to each other and to other properties of the elements that produce them is not very evident. However, on any theory of the emission of waves the wave-length increases with increase of the linear dimensions of the segment or portion of matter producing them. Consider therefore an isolated body, to be definite a rectangular bar of steel say, producing vibrations. Waves of different lengths may be given off simultaneously, but the length of each will be proportional to the length of the segment producing it. If the linear dimensions of the bar be increased, the other properties

remaining unchanged, the wave-length of each set of vibrations will be correspondingly increased, the total increase in each case being proportional to the wave-length itself. Now suppose the bar in the midst of a great number of others of either the same or of different material and all moving at random with considerable velocity. Many collisions will take place; part of the energy of the system becoming internal energy of the bar in question and thereby increasing its linear dimensions and consequently the wave-lengths of its vibrations. Further, the more numerous the bars in a given space the more frequent in the same proportion will be the collisions and therefore the greater will become the internal energy of the bar, its linear dimensions and the wave-lengths of its vibrations. Again, of two bars under the supposed conditions, that one which has the greater coefficient of linear expansion will suffer the greater change in the lengths of its waves.

Since, at any given temperature, the coefficient of expansion of a bar of metal remains constant, so far as is known, no matter how small the bar, and since also the coefficient of expansion of a porous bar, or one bored to any extent and in any direction, is the same as that of a solid bar of the same substance, it would seem on pushing these ideas to the limit, that the coefficient of expansion of a substance in the solid form is also more or less nearly a measure of the expansion of its smallest parts or molecules. Nor does it seem unreasonable to suppose, when these molecules are moving rapidly and in the midst of many others, as they are when the substance is in the form of a gas, that their collisions would lead to an increase of the internal energy of the molecules themselves and consequently to their expansion and to an increase in the wave-lengths of their vibrations. At any rate if the particles producing light-vibrations have properties like those of appreciable masses of the same substance, then the above considerations in regard to the steel bar offer a possible explanation of many, and probably the most important, of the observed facts in regard to the shifts of the spectral lines. In this way is explained why the wave-lengths should always increase with

increase of pressure, and why it is independent of the partial pressure of the gas to which the lines are due. It is also evident that the shifts of the lines should be proportional to their wave-lengths, and greatest for those substances which have the greatest coefficient of linear expansion. This idea offers at least a partial explanation as to why the shifts of the lines should be, as experiment shows them, practically independent of temperature when the pressure is kept constant, since in this case the greater velocity of the particles due to increase of temperature is offset in a measure by the corresponding rarefaction, so that the increase of internal energy of the molecules *due to collisions* may be but slightly, if at all, changed by change of temperature alone. Still an increase of the temperature alone almost certainly increases the amplitudes of the vibrations—the lines become more intense—and it is difficult to see why the internal energy of the molecule should not at the same time be so increased as to make its linear dimensions greater. This, however, it seems would make the wave-lengths greater, a result that is not in accord with experiment.

Why different series of lines of the same element should shift differently is far from evident, and it is with the greatest hesitation that I offer the slightest suggestion in regard to it.

Conceivably the vibrating particles may expand differently in different directions, or possibly the different series of lines may be due to entirely different molecular complexes of very different coefficients of expansion. This latter idea seems to be supported in a measure by the following considerations: The melting point of a substance and its coefficient of expansion both appear to be in some sense inversely proportional to the ability of its particles to resist external influences; and those molecular complexes least capable of resisting external influences may, therefore, at the temperature of the electric arc, be subject to dissociation and possibly to other changes as well. Now it happens that those substances which furnish clearly marked series of lines, as do sodium, potassium, cadmium, mercury, and others, are those whose melting points are among the lowest and

whose coefficients of expansion are the greatest. Should dissociation take place, it is clear that the dissociated parts must be either less subject to external influences or else less powerfully acted upon than are the undissociated parts, else they too would still further dissociate, which process evidently stops somewhere. In either case a smaller coefficient of expansion of the parts might be expected than is that of the undissociated portions. Again it seems but natural to suppose the dissociation taking place along planes of symmetry, should such planes exist, or at least in a manner that would leave the parts with linear dimension approximately but half those of the original whole. Supposing, then, the coefficients of expansion, or better possibly, the amounts of energy used in producing expansion of the parts to be such as to cause these coefficients to be to each other as the linear dimensions of the particles themselves, we have at once an explanation of the 1:2:4 relation of the shifts of the series.

This also suggests a possible explanation of the fact that analogous elements, as rubidium and caesium, tin and lead, and others give lines that shift proportionately to the cube roots of their atomic weights, since (if the atoms are of about the same density) the cube roots of their weights are to each other as their linear dimensions. Or, on the other hand, if, as seems possible, the shifts of the lines are to each other as the linear dimensions of the particles to which they are due, it follows that analogous elements—elements of the same half of a Mendelejeff group—differ from each other in the main because of the difference in the linear dimensions of their atoms.

Again I wish to say that these suggestions are offered with the greatest hesitation (the assumptions made are not yet justified), and only with the hope that they may be of some service in mapping out further investigations along this line of spectrum analysis.

HISTORY OF THE PRESENT INVESTIGATION.

The present investigation was begun in February 1895 by Dr. J. F. Mohler and myself, and continued as joint work till

December of the same year. Our accumulated results on twenty-three elements were then published in the *ASTROPHYSICAL JOURNAL*, December 1895, and likewise, though in a much less complete form, in the Johns Hopkins University *Circulars* for February 1896. A preliminary account of it had also been given by Dr. Mohler at the Springfield (1895) meeting of the American Association for the Advancement of Science.

Dr. Mohler then examined alone the effect of very low pressures on a few of the elements whose behavior at high pressure was already known, and published his results in the *ASTROPHYSICAL JOURNAL* of October 1896, and I, working independently, extended the examination at high pressures to a number of additional elements, the results of which appeared in the November 1896 number of the same *JOURNAL*.

The present paper, though including all that has been done in this line, except Mohler's work at low pressure, contains much that is new—the history, so far as there is one, of the subject; the behavior of several additional elements (the metallic elements are now practically exhausted); the behavior of different groups of analogous lines, like those of copper and iron, and in particular the different series of lines as furnished by lithium, sodium, zinc, and others; and also a fuller study of several of the elements, iron, zinc, copper, cadmium, among others previously studied by Mohler and myself.

DESCRIPTION OF PLATE XVII.

Some idea of the effect of pressure on spectral lines may be got from the accompanying plate, which is taken from a few of the negatives obtained during the course of my work. I shows the pair of sodium lines λ 3302.504 and λ 3303.119. The inner portion was taken at a pressure of eight and one-half atmospheres and the outer portion at one atmosphere. On the outside the unsymmetrical nature of these lines is clearly seen, the spreading being to the violet; yet, as shown by the plate, the lines under pressure are greatly shifted towards the red of the spectrum. II is from the New Concord meteorite, the inner portion being

taken at a pressure of twelve atmospheres. This shows several of the iron lines that shift to a greater extent than do others of the same element. It shows also a portion of a cyanogen band, whose lines are not appreciably displaced. Further, it shows that the lines under pressure reverse more readily than do the same lines at normal pressure. III, the inner portion of which was formed at a pressure of seven atmospheres, shows the great difference in the shifts of two classes of copper lines. In this case the plate was taken from an arc formed between a copper and a brass rod, the brass forming the lower and positive pole. IV shows the potassium lines $\lambda 4044.294$ and $\lambda 4047.338$, which are greatly shifted. The small line between them is due to iron. The pressures were for the outsides and the middle, one and eight and a half atmospheres respectively. V gives the rubidium lines (in the cyanogen band), the shifts of which are very evident. In this case the pressures were also eight and a half and one atmospheres. In fact, V and IV are but different portions of the same plate.

In closing I wish to thank Professor Rowland and Dr. Ames, under whose direction this work was conducted, not only for their assistance every time it was needed, but also for the thoroughly kind and helpful manner in which it was invariably given.

My thanks are also due to Mr. L. E. Jewell for the willingness with which he often brought his extensive knowledge of the spectra of the elements to my aid.

BIOGRAPHICAL SKETCH.

W. J. Humphreys was born in Monroe County, West Virginia, and educated at Washington and Lee University (A. B. 1886 and C. E. 1888), University of Virginia (Graduate in the Schools of Chemistry and the School of Physics 1889) and the Johns Hopkins University (Ph.D. 1897).

He taught Physics and Mathematics at the Miller School, Virginia, four years, 1889-1893, had the chair of Physics and Chemistry in Washington College, Maryland, during the session of 1893-'94, entered, on an Honorary Scholarship (Virginia), the Johns Hopkins University at the opening of the session of 1894-'95 for a graduate course in Physics, Chemistry and Mathematics, was given a Fellowship in Physics for 1895-'96 and made Fellow by Courtesy and appointed Student Assistant in Physics for 1896-'97.

At present (November, 1897) he is Instructor in Physics at the University of Virginia.

